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Determination of selected parabens, benzophenones, triclosan and triclocarban in agricultural soils after and before treatment with compost from sewage sludge: A lixiviation study

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ABSTRACT

An accurate and sensitive method for the determination of selected EDCs in soil and compost from wastewater treatment plants is developed and validated. Five parabens, six benzophenone-UV filters and the antibacterials triclosan and triclocarban were selected as target analytes. The parameters for ultrasound-assisted extraction were thoroughly optimized. After extraction, the analytes were detected and quantified using ultra-high performance liquid chromatography tandem mass spectrometry. Ethylparaben (ring–$^{13}C_6$ labelled) and deuterated benzophenone (BP-d_{10}) were used as internal standards. The method was validated using matrix–matched calibration and recovery assays with spiked samples. The limits of detection ranged from 0.03 to 0.40 ng g^{-1} and the limits of quantification from 0.1 to 1.0 ng g^{-1}, while precision in terms of relative standard deviation was between 9% and 21%. Recovery rates ranged from 83% to 107%. The validated method was applied for the study of the behavior of the selected compounds in agricultural soils treated and un-treated with compost from WWTP. A lixiviation study was developed in both agricultural soil and treated soil and first order kinetic models of their disappearance at different depths are proposed. The application of organic composts in the soil leads to an increase of the disappearance rate of the studied compounds. The lixiviation study also shows the risk of pollution of groundwater aquifers after disposal or waste of these EDCs in agricultural soils is not high.

1. Introduction

The production of compost from sewage sludge produced in wastewater treatment plants (WWTP) is an efficient way to reduce this hazardous waste. Compost can be used as organic fertilizer in grows and forests, as substrate for regeneration of contaminated soils or as artificial soil in construction. Recycling urban wastes leads fewer residues stored in landfills. These residues are a high risk for the environment, because toxic substances can lixiviate and contaminate groundwater and aquifers. The use of compost also entails important economic benefits because the need of water, fertilizers and pesticides is reduced. The United States Environmental Protection Agency (US-EPA) recommends the use of compost due its multiples environmental benefits [1].

The composting processes must be made adequately for an efficient and safe use of composts from sewage sludge. The compost must be free of toxic pollutants and pathogens. The European Union (UE) has fixed the requirements that compost must meet for its use in a safe mode. These requirements are regulated by means of the Directive 2008/98/EC, also known as the EU waste framework Directive [2]. The US-EPA has regulated the use of compost and bio-soils, in this case by means of the Standards for Use or Disposal of Sewage Sludge (40 CFR, Part 503, under the Clean Water Act) [3].

However, the wide use of personal care products (PCPs) and other products related with human activities has led the contamination of groundwater with these new contaminants [4]. Generally, these compounds come to the environment through inadequately treated wastewaters. The use of contaminated compost can be a great risk for the environment and human health. Therefore, the availability of adequate analytical methods for the analysis of PCPs in agricultural soils, composts and composted soils is of great interest. These methods will allow the realization of future studies of the different composting processes and the study of the behavior of these new pollutants after the application of contaminated compost in soils.

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Table 1
Optimized SRM conditions and retention times for the studied analytes.

Analyte	ESI	SRM1[a] (Da)	CV/CE (V)	SRM2[b] (Da)	CV/CE (V)	t_R (min)
MPB	–	151.1 > 91.8	38/22	151.1 > 135.9	38/14	0.81
EPB-$^{13}C_6$	–	171.2 > 98.0	36/24	171.2 > 97.9	44/22	0.83
EPB	–	165.1 > 91.9	38/24	165.1 > 136.6	38/16	0.86
PPB	–	179.1 > 91.9	42/24	179.1 > 136.1	42/16	0.95
BPB	–	193.2 > 91.9	42/24	193.2 > 136.1	42/16	1.19
BP-2	–	245.1 > 134.8	40/16	245.1 > 108.8	40/22	0.64
BP-1	+	214.9 > 136.8	2/18	214.9 > 80.8	2/32	0.80
4-OH-BP	+	199.0 > 120.8	36/20	199.0 > 104.8	36/18	0.82
Ph-PB	–	213.0 > 92.9	18/28	213.0 > 136.0	18/16	0.91
BP-8	+	244.9 > 120.8	14/20	244.9 > 150.8	14/20	2.24
BP-6	+	275.0 > 150.9	14/18	275.0 > 128.7	14/18	2.53
BP-d_{10}	+	193.1 > 109.8	18/16	193.1 > 81.8	18/30	3.72
BP-3	+	229.0 > 150.8	4/20	229.0 > 104.9	4/18	4.45
TCS	–	287.0 > 141.8	22/32	287.0 > 160.8	22/40	3.40
TCB	–	313.1 > 150.9	2/14	313.1 > 126.2	2/14	5.39
MCA	–	294.2 > 258.0	2/16	294.2 > 213.9	2/20	0.93

CV = cone voltage; CE = collision energy; t_R = retention time.
[a] SRM1 = transition used for quantification.
[b] SRM2 = transition used for confirmation.

In the present work, three families of emerging pollutants, preservatives (parabens), a family of uv-filters (benzophenones) and two biocides (triclosan and triclocarban) have been studied. These substances were selected for their interest and because to date there is few data about their behavior and fate in the environment. Parabens (PBs) are widely used as preservatives in personal care products, and they are considered as possible endocrine disruptors [5,6]. Benzophenones, mainly BP-3, because they can absorb the UV radiation, are used as components of sunlockers, lotions and hair sprays. Some of these UV filters have been reported to possess significant estrogenic activity [7,8]. Triclosan (TCS) and triclocarban (TCB) are two common antimicrobial and biocides used in shampoo, toothpaste and many other daily products, which in the present are reported as also possible endocrine disruptors and their fate in the environment must be investigated [9–14]. Dispose of multi-residue methods for the analysis of the mayor number of pollutants in agricultural soils, compost from sewage sludge or mixtures of them, is very important due the lowest costs per analysis and less analysis time required obtaining more information about the real contamination of a sample.

In this sense, these pollutants has been widely found in a large amount of environmental matrices, including waters [15–19] or solid matrices such as sewage sludge, soils or sediments [20–28]. Different analytical techniques have been employed, being gas chromatography (GC) or liquid chromatography (LC) coupled to mass spectrometry (MS) the preferred. LC with ultraviolet detection [29] has been also used for the determination of parabens in solid environmental samples. The main disadvantage of GC–MS is the need of a derivatization procedure that makes the sample treatment slower than LC–MS analysis; however, similar results and performance are obtained with both techniques. To date, very few methods employing triple quadrupole MS have been proposed [25–28]. The use of MS/MS increases the specificity and selectivity of the detection method, particularly when analyzing dirty and complex matrices such as sewage sludge and compost. For this reason, triple quadrupole MS in the selected reaction monitoring (SRM) mode has been selected to simplify sample treatment over other previously proposed methods. Regarding sample treatment, well-known extraction techniques have been successfully applied for extraction and isolation of EDCs in solid samples. Molecular imprinted polymers (MIPs), solid phase extraction (SPE), pressurized liquid extraction (PLE), ultrasound-assisted extraction (USE) or microwave-assisted extraction (MAE) have been used.

In this context, it is important to remark that, to our knowledge, none of the existing methods are focused on the multiclass determination of EDCs in compost samples and even less in amended agricultural soil samples, which are complex environmental matrices mainly due to its high content of organic matter. In the present work, a procedure to carry out the simultaneous extraction of three class of emerging pollutants in these matrices using ultrasound assisted extraction (UAE) and analysis of the extracts by ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) has been validated. Furthermore, the method was applied to the study of the behavior of the selected compounds in soils and amended soils with compost from WWTP sewage sludge. A comparative study of the lixiviation and disappearance of the analytes in both amended and non-amended soils was performed. Kinetic models have been subsequently constructed at different depths with the obtained data, in order to obtain a better knowledge of the potential environmental impact of the studied compounds.

2. Experimental

2.1. Chemicals and reagents

All reagents were analytical grade unless otherwise specified. Water (18.2 MΩ cm) was purified using a Milli-Q system from Millipore (Bedford, MA, USA). Methylparaben (MPB), ethylparaben (EPB), propylparaben (PPB), phenylparaben (Ph-PB) and butylparaben (BPB) were supplied by Alfa Aesar (Massachusetts, MA, USA). Triclosan, triclocarban, benzophenone-1 (BP-1), benzophenone-2

Table 2
Evaluation of the experimental design results.

Compound	R^{2}[(a)] (%)	Extraction solvent volume (mL)			Extraction time (min.)		
		Optimal	Significant[(b)]	Effect	Optimal	Significant[(b)]	Effect
Results for soil samples							
Parabens	99.88	15	Yes	+	25	Yes	+
Benzophenones	99.95	15	No	+	25	Yes	+
TCS + TCB	99.67	15	Yes	+	25	Yes	+
Results for compost samples							
Parabens	99.82	15	No	+	25	Yes	+
Benzophenones	99.96	15	No	+	25	Yes	+
TCS + TCB	99.78	15	Yes	+	25	No	+

[a] Extimation of the fit of the experimental results to the proposed model.
[b] A variable is considered significant when $P_{value} < 0.05$.